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SUBMILLIMETER LABORATORY INVESTIGATIONS:

SPECTROSCOPY AND COLLISIONS

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Our group was the first to extend studies of the rotational spectra of small and fundamental gas-phase molecules from the microwave into first the millimeter-wave and subsequently the submillimeter-wave region of the spectrum (King & Gordy 1953; Helminger et al. 1970, 1983). A bibliography of the many molecules studied in the laboratory, consisting of over 400 papers, is available upon request. The results presented in these papers provide the basis for the identification of a significant fraction of the interstellar spectral lines. For interstellar molecules previously detected at lower frequencies, our submillimeter-wave spectra provide the opportunity for additional study of these species under warmer conditions.

For the duration of this proposal and previously, we have concentrated on those molecules with the largest number of interstellar spectral lines. These species are so-called internal rotors, in which one portion of the molecule (normally a methyl ( $\text{CH}_3$ ) group) undergoes a hindered rotational motion with respect to the other portion of the molecule. The hindered rotational motion, known as torsion, leads to quantized states typically separated by 50–100 K and labeled with a quantum number  $v_t = 0, 1, 2, \dots$ . For the three-fold case, each torsional state is also split into two substates – designated *A* and *E*. The existence of these extra states compared with normal molecules is of great use for probing warm regions with temperatures too low to excite normal vibrations but higher than the ambient interstellar medium. Strong interactions between torsional and rotational motion, however, make the spectra of some internal rotors quite complex and, for many years, it was very difficult if not impossible to analyze their spectra to microwave accuracy. Without such a detailed analysis, it is not possible to predict the frequencies of the many lines not measured in the laboratory with sufficient precision for use by radio astronomers, nor to determine intensities.

More than a decade ago (De Lucia et al. 1989), we showed how an extended Hamiltonian based on the internal axis method (IAM; Lees & Baker 1968) can be used to analyze the spectrum of methanol ( $\text{CH}_3\text{OH}$ ), a well-known interstellar molecule and perhaps the best known internal rotor, to microwave accuracy. Since that time, we and other groups have extended and refined the method to study methanol, its isotopomers, and similar internal rotors. In our most recent work on methanol, we studied the rotational-torsional spectrum in the frequency range 0.55–1.2 THz and observed over 450 new spectral lines belonging to 14 Q branches and 3 R branches in the lowest three torsional states ( $v_t = 0-2$ ; Belov et al. 1995). The high frequency experiments were done in the laboratory of Gisbert Winnewisser in Cologne, Germany. The newly measured lines have been added to previously measured transitions to comprise a global data set, which has been fit to near-microwave accuracy via our extended internal axis method. The spectroscopic constants determined in the fit can be used to predict the frequencies of many lines not measured in the laboratory. A more recent update of some of the measured and predicted methanol frequencies has been provided by Xu and Lovas (1997). Although methanol is a well-known and widespread interstellar molecule, its sulfur analogue – methyl mercaptan ( $\text{CH}_3\text{SH}$ ) – has only been detected in one source, to the best of our knowledge. We (Bettens et al. 1999) have recently measured and analyzed the rotational-torsional spectrum of this internal rotor through 550 GHz in frequency so that radio astronomers have a better chance of finding it.

Methyl formate ( $\text{HCOOCH}_3$ ) is almost as well-known an interstellar molecule as methanol, although its many interstellar spectral lines appear to be confined to so-called Hot Cores (high-mass star formation regions) inside dense clouds. We have worked on the dense rotational-torsional spectrum of methyl formate for many years. Our first analyses were based on a perturbative approach known as the principal axis method, or PAM (see, e.g., Plummer et al. 1986). We were quite successful in our analysis of the  $v_t=0$ , *A* state, and have published accurate predictions through 600 GHz. The analogous spectrum of the  $v_t=0$  *E* state has been more difficult to analyze, and our original analysis was useful only through 300 GHz. Switching to the IAM approach used for methanol has proved most helpful, and we (Oesterling et al. 1999) have most

recently succeeded in fitting both the *A* and *E* spectra of  $v_t=0$  through 600 GHz in frequency. Many additional predicted frequencies through 700 GHz have been provided. Although it has not yet been detected in space, the symmetric deuterated isotopomer of methyl formate ( $\text{DCOOCH}_3$ ) is of possible interest to radio astronomers because it can yield information about fractionation in hot cores. We have measured and analyzed its spectrum through 377 GHz using the internal axis method (Oesterling et al. 1995).

We have also worked on the spectra of molecules with two rotating methyl groups; these include dimethyl ether ( $\text{CH}_3\text{OCH}_3$ ) and acetone ( $\text{CH}_3\text{COCH}_3$ ). Dimethyl ether is similar to methyl formate in that its many interstellar lines are detected towards Hot Cores. We measured a large number of new lines in the frequency range 100-550 GHz and incorporated the new measurements into a large data set, which was analyzed by a perturbative method (Groner et al. 1998). The spectral constants allowed us to predict accurately the frequencies of 6000 additional lines through 600 GHz. We have also recently finished an analogous study of the rotational-torsional spectrum of acetone (Groner et al. 2002).

Not all polyatomic molecules are internal rotors, of course, and we have studied a significant number of normal rigid species. One of the more important ones in the last five years is ethylene oxide ( $\text{c-C}_2\text{H}_4\text{O}$ ; Pan et al. 1998).

Following a sabbatical of the PI in the laboratory of Gisbert Winnewisser (Cologne, Germany), a secondary collaboration was started. In recent years, the collaboration has mainly involved the THz and near THz (500-1200 GHz) rotational spectra of diatomic radicals produced in discharge sources. These species include CN, SO, NO, SH, SD, PH, and CF (e.g., Klisch et al. 1996, 1998, 1999; Morino et al. 2000). The radicals CN, SO, and NO are well-known interstellar species and their high frequency spectra are useful for study in warm regions associated with star formation. The radicals SH, SD, PH, and CF remain to be detected in space.

Since the rotational levels of interstellar molecules are not generally in thermodynamic equilibrium, the analysis of spectral intensities requires a knowledge of the inelastic collisions that populate the rotational levels. In our laboratory, we have studied rotationally inelastic collision rates through two approaches: indirect and indirect. The indirect approach involves the laboratory study of pressure broadening of rotational transitions at very low temperatures. Given a known potential surface, quantum scattering techniques can be used to simulate laboratory pressure broadening. If the simulation is accurate, the same techniques can be utilized to calculate inelastic collision rates confidently. Studies of low temperature  $\text{H}_2\text{CO-H}_2$  and  $\text{CO-H}_2$  collisions have been pursued by this method (Mengel et al. 2001). The indirect approach suffers somewhat from difficulties in simulating pressure-broadening data due most probably to uncertainties in the intermolecular potentials. The direct approach involves double resonance (pump-probe) techniques (Everitt & De Lucia 1995). This approach is difficult experimentally, particularly if cross sections for specific state-to-state processes are desired. Initially, this technique was used in our laboratory to study rotationally inelastic collisions of molecules pumped into excited vibrational states, although these rates should be almost the same as ground state rates. More recently, we have begun to study the collisional relaxation of molecules cooled by our collisional cooling technique that are pumped into excited rotational states. The  $\text{H}_2\text{S-He}$  system (Ball & De Lucia 1998; De Lucia et al. 1998) was measured over the temperature range 1-40 K and yielded data on the inelastic collisions connecting the rotational states  $1_{1,0}$  and  $1_{0,1}$ . The  $\text{NO-He}$  system (Ball & De Lucia 1999) was studied at 4.2 K and yielded absolute cross sections for a variety of  $\Delta J$  and  $\Delta F$  collisional processes.

We have also investigated the low temperature collisions of the molecular ions  $\text{CO}^+$  and  $\text{HCO}^+$  with CO and  $\text{H}_2$ . Initial work on the pressure broadening of collisionally-cooled  $\text{HCO}^+$  (Pearson et al. 1995) by collisions with  $\text{H}_2$  has been followed by time-dependent studies of the collisional relaxation of  $\text{CO}^+$  and  $\text{HCO}^+$  following formation via electron bombardment of precursor gases (De

Lucia et al. 1998). We have recently finished a study in which we utilize the direct (pump-probe) technique to probe  $\text{HCO}^+$  collisions with  $\text{H}_2$  directly after the  $\text{HCO}^+$  is thermalized (Oesterling, De Lucia, & Herbst 2001). Although our collisional experiments have not yet had the impact in the astronomical community of our spectroscopic experiments, we hope that in the near future our detailed cross sections for inelastic collisions of both cold neutrals and ions with  $\text{H}_2$  will begin to aid the analysis of interstellar rotational lines.

### Technical Approach/Methodology

Currently, millimeter-wave and submillimeter-wave spectroscopy is conducted in our laboratory on several different types of spectrometers. Our standard spectrometer utilizes the output of a phase-locked klystron operating in the 40-60 GHz region, which is sent into a crossed-waveguide harmonic generator, or "multiplier" (Helminger et al. 1983). The high frequency millimeter- and submillimeter-wave radiation is transmitted via quasi-optical techniques through an absorption cell and then onto a detector, which is either an InSb hot electron bolometer cooled to 1.4 K or a Si bolometer cooled to 0.3 K. The detector response is sent to a computer for measurement and analysis. The frequency range produced and detected in this manner goes from 80 GHz to upwards of 1 THz. Spectra are normally taken with source modulation, with line frequencies typically measured to an accuracy of 50-100 kHz. Higher accuracy is available when needed.

Recently, we developed a new, broad-band spectrometer in our laboratory based on a free-running backward wave oscillator (BWO) of Russian manufacture as the primary source of radiation (Petkie et al. 1997). The so-called FASSST (fast-scan submillimeter spectroscopic technique) system uses fast-scan and optical calibration methods rather than the traditional locking techniques. The output power from the BWO is split such that 90% goes into the absorption cell while 10% is coupled to a 40-meter Fabry-Perot cavity, which yields fringes for frequency measurement. Results from this spectrometer on the spectrum of nitric acid ( $\text{HNO}_3$ ) show that 100 GHz of spectral data can be obtained in 5 seconds with a measurement accuracy of 50 kHz. Currently, the frequency range of the FASSST system in our laboratory is roughly 100–700 GHz.

The use of more traditionally phase-locked Russian BWO's, along with frequency multiplication, has allowed the group in Cologne, Germany, headed by G. Winnewisser, to obtain and characterize radiation at frequencies through 1.7 THz (Winnewisser, private communication). With laser sideband techniques, Winnewisser has produced frequencies through 2 THz. Some of our work on this project requiring such high frequencies has been undertaken in Cologne, in collaboration with the group there.

A wide variety of different absorption cells are used in our spectroscopic studies. For standard, non-reactive species with a significant vapor pressure at room temperature, we use glass cylindrical cells. For molecules that require a high temperature to produce sufficient vapor pressure or for the study of molecules in excited vibrational states, we are equipped with high temperature cells. For radicals and molecular ions, we have both microwave and D. C. glow discharges. Our magnetically-confined glow discharge technique for the study of molecular ions (De Lucia et al. 1983) at temperatures down to 77 K increases the ion signal by up to two orders of magnitude over conventional discharges and has been widely adopted. For the study of molecules at exceedingly low temperatures, we have developed the collisional cooling technique, in which species are bled into a cell of cryogenically cooled helium or hydrogen, and cooled before condensing onto the walls of the apparatus. Used initially for neutral species, the technique has been adopted for molecular ions (Pearson et al. 1995) and utilized to study pressure broadening of the ion  $\text{HCO}^+$  by  $\text{H}_2$  in the temperature range 11-30 K. We have also developed ion cells that operate at or near thermodynamic equilibrium at somewhat higher temperatures.

The spectral absorption lines measured in our spectrometers arise from changes in the rotational energy levels of molecules. The complexity of a rotational spectrum is dependent upon factors such as the structure of a molecule, its rigidity, and its electronic symmetry. We have studied and are equipped to analyze molecules with rotational spectra of varying degrees of complexity.

## References

- Ball, C. D. & De Lucia, F. C. 1998, "Direct Measurement of Rotationally Inelastic Cross Sections at Astrophysical and Quantum Collisional Temperatures," *Phys. Rev. Letters*, 81, 305
- Ball, C. D. & De Lucia, F. C. 1999, "Direct Observation of A Doublet and Hyperfine Branching Ratios for Rotationally Inelastic Collisions of NO-He at 4.2K," *Chem. Phys. Lett.*, 300, 227
- Belov, S. P., Winnewisser, G., & Herbst, E. 1995, "The High Resolution Rotational-Torsional Spectrum of Methanol from 0.55 to 1.2 THz," *J. Mol. Spectrosc.*, 174, 253
- Bettens, F. L., Sastry, K. V. L. N., Herbst, E., Albert, S., Oesterling, L. C., & De Lucia, F. C. 1999, "The Millimeter- and Submillimeter-wave Spectrum of Methyl Mercaptan ( $\text{CH}_3\text{SH}$ )," *ApJ*, 510, 789
- De Lucia, F. C., Herbst, E., Anderson, T., & Helminger, P. 1989, "The Analysis of the Rotational Spectrum of Methanol to Microwave Accuracy," *J. Mol. Spectrosc.*, 134, 395
- De Lucia, F. C., Herbst, E., Oesterling, L. C., Ball, C. D., & Albert, S. 1998, "Submillimeter-wave Investigations of 'Space in a Bottle' – Spectroscopy and Collisions from 1 – 1000 K," NASA Laboratory Space Science Workshop (Center for Astrophysics, Volume of Program, papers, & abstracts), 126
- De Lucia, F. C., Herbst, E., Plummer, G. M., & Blake, G. A. 1983, "The Production of Large Concentrations of Molecular Ions in the Lengthened Negative Glow Region of a Discharge," *J. Chem. Phys.*, 78, 2312
- Everitt, H. O., & De Lucia, F. C. 1995, "Rotational Energy Transfer in Small Polyatomic Molecules," *Adv. At. Mol. Opt. Phys.*, 35, 331
- Groner, P., Albert, S., Herbst, E., & De Lucia, F. C. 1998, "Dimethyl Ether: Laboratory Assignments and Predictions through 600 GHz," *ApJ*, 500, 1059.
- Groner, P., Albert, S., Herbst, E., De Lucia, F. C., Lovas, F. J., Drouin, B. J., & Pearson, J. C. 2002, "Acetone: Laboratory Assignments and Predictions thorough 620 GHz for the Vibrational-Torsional Ground State," *ApJS*, 142, 145
- Helminger, P., De Lucia, F. C., & Gordy, W. 1970, "Extension of Microwave Absorption Spectroscopy To 0.37-mm Wavelength," *Phys. Rev. Lett.*, 25, 1397
- Helminger, P., Messer, J. K., & De Lucia, F. C. 1983, "Continuously Tunable Coherent Spectroscopy for 0.1-1.0 THz Region," *Appl. Phys. Lett.*, 42, 309
- Klisch, E., Belov, S. P., Winnewisser, G., & Herbst, E. 1999, "Transitions between Hund's coupling cases for the  $X^2\Pi$  State of NO," *Mol. Phys.*, 97, 65
- Klisch, E., Klaus, Th., Belov, S. P., Dolgner, A., Schieder, R., Winnewisser, G., & Herbst, E. 1996, "The Rotational Spectrum of SH and SD," *ApJ*, 473, 1118
- Klisch, E., Klein, H., Winnewisser, G., & Herbst, E. 1998, "Laboratory Rotational Spectrum of PH ( $N = 2 \leftarrow 1$ ) in the 1 THz Region," *Z. Naturforsch.*, 53a, 733.
- Lees, R. M., & Baker, J. G. 1968, "Torsion-Vibration-Rotation Interactions in Methanol. I. Millimeter-wave Spectrum," *J. Chem. Phys.*, 48, 5299
- Mengel, M., De Lucia, F. C., & Herbst, E. 2001, "Rate coefficients for rotationally inelastic collisions of CO with  $\text{H}_2$ ," *Can. J. Phys.*, 79, 589
- Morino, I., Yamada, K. M. T., Belov, S. P., Winnewisser, G., & Herbst, E. 2000, "The CF Radical: Terzhertz Spectrum and Detectability in Space," *ApJ*, 532, 377
- Oesterling, L. C., Albert, S., De Lucia, F. C., Sastry, K. V. L. N., & Herbst, E. 1999, "The Millimeter- and Submillimeter-wave Spectrum of Methyl Formate ( $\text{HCOOCH}_3$ )," *ApJ*, 521, 255
- Oesterling, L. C., & De Lucia, F. C. 1998, "Millimeter-wave Time-Resolved Studies of the Formation of  $\text{CO}^+$  by Electron Impact," *Ohio State Intern. Symp. Molec. Spectrosc.*, 53, 218
- Oesterling, L. C., Ferguson, D. W., Herbst, E., & De Lucia, F. C. 1995, "The Millimeter- and Submillimeter-wave Spectrum of Symmetric Mono-deuterated Methyl Formate ( $\text{DCOOCH}_3$ )," *J. Mol. Spectrosc.*, 172, 469
- Oesterling, L. C., De Lucia, F. C., & Herbst, E. 2001, "Millimeter-wave time-resolved studies of  $\text{HCO}^+-\text{H}_2$  inelastic collisions," *Spectrochim. Acta A*, 57, 705

Pan, J., Albert, S., Sastry, K. V. L. N., Herbst, E., & De Lucia, F. C. 1998, "The Millimeter- and Submillimeter-wave Spectrum of Ethylene Oxide (c-C<sub>2</sub>H<sub>4</sub>O)," *ApJ*, 499, 51

Pearson, J. C., Oesterling, L. C., Herbst, E., & De Lucia, F. C. 1995, "Pressure Broadening of Gas Phase Molecular Ions at Very Low Temperature," *Phys. Rev. Letters*, 75, 2940

Petkie, D. T., Goyette, T. M., Bettens, R. P. A., Belov, S. P., Albert, S., Helminger, P., & De Lucia, F. C. 1997, "A Fast Scan Submillimeter Spectroscopic Technique," *Rev. Sci. Instr.*, 68, 1675

Plummer, G. M., Herbst, E., De Lucia, F. C., & Blake, G. A. 1986, "The Laboratory Millimeter-wave Spectrum of Methyl Formate in its Ground Torsional *E* State," *ApJS*, 60, 949

Xu, L.-H., & Lovas, F. J. 1997, "Microwave Spectra of Molecules of Astrophysical Interest. XXIV. Methanol (CH<sub>3</sub>OH and <sup>13</sup>CH<sub>3</sub>OH)," *J. Phys. Chem. Ref. Data*, 26, 17

### *PAPERS SUPPORTED BY NASA GRANT*

1. Pan, J., Albert, S., Sastry, K. V. L. N., Herbst, E., & De Lucia, F. C. 1998, "The Millimeter- and Submillimeter-wave Spectrum of Ethylene Oxide ( $c\text{-C}_2\text{H}_4\text{O}$ )," *ApJ*, 499, 517
2. Groner, P., Albert, S., Herbst, E., & De Lucia, F. C. 1998, "Dimethyl Ether: Laboratory Assignments and Predictions through 600 GHz," *ApJ*, 500, 1059.
3. Klisch, E., Klein, H., Winnewisser, G., & Herbst, E. 1998, "Laboratory Rotational Spectrum of PH ( $N = 2 \leftarrow 1$ ) in the 1 THz Region," *Z. Naturforsch.*, 53a, 733.
4. Bettens, F. L., Sastry, K. V. L. N., Herbst, E., Albert, S., Oesterling, L. C., & De Lucia, F. C. 1999, "The Millimeter- and Submillimeter-wave Spectrum of Methyl Mercaptan ( $\text{CH}_3\text{SH}$ )," *ApJ*, 510, 789.
5. Oesterling, L. C., Albert, S., De Lucia, F. C., Sastry, K. V. L. N., & Herbst, E. 1999, "The Millimeter- and Submillimeter-wave Spectrum of Methyl Formate ( $\text{HCOOCH}_3$ )," *ApJ*, 521, 255.
6. Morino, I., Yamada, K. M. T., Belov, S. P., Winnewisser, G., & Herbst, E. 2000, "The CF Radical: Terahertz Spectrum and Detectability in Space," *ApJ*, 532, 377
7. Butler, R. A. H., De Lucia, F. C., Petkie, D. T., Møllendal, H., Horn, A., & Herbst, E. 2001, "The Millimeter- and Submillimeter-wave Spectrum of Glycolaldehyde ( $\text{CH}_2\text{OHCHO}$ )," *ApJS*, 134, 319
8. Mengel, M., De Lucia, F. C., & Herbst, E. 2001, "Rate coefficients for rotationally inelastic collisions of CO with  $\text{H}_2$ ," *Can. J. Phys.*, 79, 589